INDIRECT MEASUREMENT OF DILUENTS
IN A MULTI-COMPONENT NATURAL GAS

RELATED PATENT APPLICATION

This application claims the benefit of U.S.
Provisional Application No. 60/458,049, filed March 27,
2003 and entitled "Indirect Measurement of Diluents in a
5   Multi-Component Natural Gas".

FIELD OF THE INVENTION

This invention relates to the field of measuring
constituent components of gas mixtures, and more
10   particularly, to measuring the concentration of diluents
in a natural gas mixture.

GOVERNMENT LICENSE RIGHTS

The U.S. Government has a paid-up license in this
15   invention and the right in certain circumstances to
require the patent owner to license others on reasonable
terms as provided for by the terms of Contract No. DE-
FC21-96MC33033 for the U.S. Department of Energy.

DESCRIPTION OF THE RELATED ART

     The concentration of nitrogen in a gas mixture is difficult to measure directly. Nitrogen has low infrared absorption characteristics, which makes infrared sensing

5   methods difficult. Also, it is chemically inert, which makes electrochemical sensing methods difficult.

     Yet, it is often desired to determine the amount of nitrogen in a particular gas mixture. For example, in a natural gas, nitrogen is a diluent and the amount of

10   nitrogen affects heating value. Experimentation has indicated that a plus or minus shift of 0.075 mole% in nitrogen concentration will produce a plus or minus shift of 1.0 BTU/SCF in standard volumetric heating value.

     U.S. Patent No. 6,604,051 B1, entitled "System and

15   Method to Determine Thermophysical Properties of a Multi-Component Gas" and U.S. Patent No. 6,704,660 entitled "A System and Method to Determine Thermophysical Properties of a Multi-Component Gas at Arbitrary Temperature and Pressure", to K. Behring and T. Morrow, describe

20   inferential methods for deriving the heating value of natural gas. These methods developed from correlation studies of the heating value of a large number of representative samples of natural gas and three independent physical parameters associated with the gas,

25   namely, the speed of sound at specified pressure and temperature and the fractional concentrations of two diluent gas components (carbon dioxide and molecular nitrogen).

     U.S. Patent No. 6,604,051 B1 further describes

30   various methods for determining the amount of molecular nitrogen in a natural gas sample. These methods are

inferential in nature in that the concentration of
nitrogen in representative natural gas mixtures, like the
gas heating value, is correlated with the speed of sound
and the carbon dioxide concentration at two independent
5   thermodynamic states. Inferential nitrogen measurement
techniques are further described in U.S. Patent
Application Serial No. 10/460,579, entitled "Indirect
Measurement of Nitrogen in a Multi-Component Natural Gas
by Heating the Gas" and in U.S. Patent Application Serial
10   No. 10/401,206, entitled "Indirect Measurement of
Nitrogen in a Multi-Component Gas by Measuring the Speed
of Sound at Two States of the Gas" filed March 27, 2003,
both continuations-in-part of U.S. Patent No.
6,604,051 B1.

BRIEF DESCRIPTION OF THE FIGURES

FIGURE 1 illustrates the characteristics of an example of a database for correlating molecular weight of natural gas to the speed of sound in the gas.

5   FIGURE 2 illustrates a method of determining the diluent concentrations in a gas mixture in accordance with the invention.

FIGURE 3 illustrates a two-channel diluent measurement system in accordance with the invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

As stated in the Background, U.S. Patent No. 6,604,051 B1, entitled "System and Method to Determine Thermophysical Properties of a Multi-Component Gas" and

5   U.S. Patent No. 6,704,660 entitled "A System and Method to Determine Thermophysical Properties of a Multi-Component Gas at Arbitrary Temperature and Pressure", describe methods for inferentially measuring heating value and energy flow rates of natural gas. U.S. Patent

10 No. 6,604,051 B1 further describes methods for inferentially measuring nitrogen. The nitrogen measurement methods are further described in U.S. Patent Application Serial No. 10/371,419, entitled "Indirect Measurement of Nitrogen in a Multi-Component Natural Gas

15 by Heating the Gas" and in U.S. Patent Application Serial No. 10/401,206, entitled "Indirect Measurement of Nitrogen in a Multi-Component Gas by Measuring the Speed of Sound at Two States of the Gas" filed March 27, 2003. These patent applications are incorporated by reference

20 herein.

Two-State Nitrogen Measurement

For inferentially measuring nitrogen, two thermodynamic states may be established by changing the

25 energy status of the test gas from a first state, at a stable and measured temperature and pressure condition, to a second stable and measurable temperature and pressure condition. The measured physical parameters include the pressure at the two states, the temperature

30 at the two states, the speed of sound at the two states, and the carbon dioxide concentration at either state.

   As explained below, with a sufficient change in
state of the gas, the correlation relationships regarding
the nitrogen content are sufficiently independent to
yield a quantitative determination of the concentration
5 of nitrogen in the test sample.

   For purposes of this description, the gas mixture is
assumed to be a natural gas, whose primary diluent
components are carbon dioxide and nitrogen. The method
is most accurate when the concentration of other diluent
10 gases is low. The method described herein may be
extended to other gases containing nitrogen, if those
gases behave similarly to natural gases.

   For the "two-state" inferential measurement of
nitrogen, it is assumed that for the particular gas
15 mixture in question, the speed of sound in the gas and
the concentration of carbon dioxide are known or
measurable by direct or indirect measurement. The
variables, X_{CO2}, X_{N2}, and S represent the carbon dioxide
concentration, nitrogen concentration, and speed of sound
20 in the gas, respectively. Temperature and pressure of
the gas are represented by T and P. Typically, these
measurements are made using a finite gas sample.

   The molecular weight of a natural gas mixture of
unknown composition is constant for the specific mixture.
25 However, the molecular weight is quantitatively unknown
because the gas constituents are not known.

   As explained in U.S. Patent No. 6,604,051 B1,
molecular weight of a gas mixture plots semi-linear with
sound speed, with the scatter in the data (about 1%)
30 being a function of the diluent concentrations.
Molecular weight (MW) may be represented by the following

equation, which relates molecular weight to speed of sound and the diluent gas concentrations:

$$MW = (A + B/S + C/S^2) * (1 + D*X_{CO2} + E*X_{N2}), \quad [1]$$

5

where MW is the molecular weight of a gas sample.

The constants A, B, C, D, and E are derived from a database containing reference gas mixtures, whose molecular weights are known. These constants are

10   functions of the gas temperature and pressure, but they are not functions of the gas composition.

FIGURE 1 summarizes a database composition range for a set of reference gas compositions. U.S. Patent No. 6,604,051 B1, incorporated by reference above, provides

15   an example of a suitable database, representing 102 unique gas compositions that fall within these ranges. For each reference gas mixture, the speed of sound can be calculated for a matrix of temperature and pressure values. The speed of sound calculations may be performed

20   using commercially available computer software such as SONICWARE, manufactured by Lomic, Inc. By applying statistical methods to the database, values of the constants can be calculated for any given temperature and pressure state.

25   The database for producing the constant values may also comprise a smaller set of reference gas compositions, selected to be representative of different molecular weights and diluent concentrations. For example, a database of nine reference gas mixtures might

30   comprise three categories of mixtures, one with high molecular weight, one with intermediate molecular weight,

and one with low molecular weight. Each category could
then comprise three mixtures, such as, one with no
diluents, one with nitrogen as the only diluent, and one
with carbon dioxide as the only diluent. An example of a

5   suitable diluent concentration for this database would be
2.0 mole% of either nitrogen or carbon dioxide or both.
Once a suitable set of reference gases is selected,
standard matrix operations for solving algebraic
equations can be used to produce values for the

10 constants. For example, the database might comprise nine
reference gases, each having a unique value of molecular
weight. The sound speeds for each of the nine gases for
a range of discrete temperature and pressure values is
calculated and stored. As stated above, this calculation

15 can be performed using commercially available software.
Then, once the temperature and pressure of the subject
natural gas is measured, interpolation can be used to
estimate the speed of sound at that state for the
reference gases. With nine values of sound speed, nine

20 values of molecular weight, and nine values of CO2 and N2
for the nine reference gases, there is sufficient
information to find the values of A, B, C, D and E at
that state. As an alternative to storing pre-calculated
sound speed values, the sound speeds for the reference

25 gases could be calculated "on the fly" for the measured
temperature and pressure, if appropriate programming is
incorporated into the run time calculations.

    The relations between the molecular weight (MW), the
diluent gas concentrations (X_{N2} and X_{CO2}), and the speed

30 of sound (S) is, for a first thermodynamic state (P_1 and
$T_{1)}$:

$$MW = \left(A_1 + \frac{B_1}{S_1} + \frac{C_1}{S_1^2}\right)\left(1 + D_2 X_{CO2} + E_2 X_{N2}\right) \qquad [2]$$

   If the speed of sound measurement is repeated at an
additional and different pressure and temperature
condition, the corresponding molecular weight expression
5 at P_2 and T_2 is:

$$MW = \left(A_2 + \frac{B_2}{S_2} + \frac{C_2}{S_2^2}\right)\left(1 + D_2 X_{CO2} + E_2 X_{N2}\right) \qquad [3]$$

   The second speed of sound measurement can be at a
different pressure or temperature or both, as compared to
10 the first speed of sound measurement. A change in either
temperature or pressure or both fulfills the requirement
that a measurement be made at a different thermodynamic
state. If the two states are too close together,
especially in pressure, the constants become closer in
15 value and the nitrogen value less determinate.
   One of the speed of sound measurements can be at
standard temperature and pressure. This speed of sound
measurement is referred to as the "standard sound speed",
where standard temperature is 60°F and standard pressure
20 is 14.73 psia.
   For sufficiently accurate and independent
measurements of the speed of sound values, S_1, and S_2,
Equations [2] and [3] may be equated to eliminate
molecular weight and to solve for the concentration of
25 nitrogen, X_{N2}, in terms of the carbon dioxide
concentration, X_{CO2},

$$X_{N2} = \frac{\left(A_2 + \frac{B_2}{S_2} + \frac{C_2}{S_2{}^2}\right)(1 + D_2 X_{CO2}) - \left(A_1 + \frac{B_1}{S_1} + \frac{C_1}{S_1{}^2}\right)(1 + D_1 X_{CO2})}{E_1\left(A_1 + \frac{B_1}{S_1} + \frac{C_1}{S_1{}^2}\right) - E_2\left(A_2 + \frac{B_2}{S_2} + \frac{C_2}{S_2{}^2}\right)} \qquad [4]$$

The separate measurement of the carbon dioxide concentration, obtained from the gas sample at either one of the test states, may now be substituted into the above
5   equation to obtain the molecular nitrogen concentration, X_{N2}.

Three-State Diluent Measurement

By supplementing the two-state measurement method
10   with a third state measurement, the need for measuring the carbon dioxide concentration in the test gas sample is eliminated. Three equations for molecular weight are obtained, and can be solved for both diluent concentrations (nitrogen and carbon dioxide).
15   FIGURE 2 illustrates this "three-state" method of determining the diluent concentrations in a sample of natural gas. Step 20 is storing a database representing a number of gas mixtures whose molecular weights and diluent constituents are known. Step 21 is modeling
20   molecular weight of any gas mixture as a function of the speed of sound in the gas, as described above.

Step 23 is measuring the speed of sound in the gas mixture at a first pressure and temperature. At that state, the equation for molecular weight is:
25

MW $= (A_1 + B_1/S_1 + C_1/S_1{}^2) * (1 + D_1 * X_{N2} + E_1 * X_{CO2})$ [5]

. In Step 24, values for the constants (A_1, B_1, ...) are calculated, using the reference gas data, which includes sound speed values at the pressure and temperature of this first state, using the techniques described above.

5   In Step 25, the speed of sound measurement is then repeated at a different state. The molecular weight is then expressed as:

$$MW = (A_2 + B_2/S_2 + C_2/S_2{}^2) * (1 + D_2*X_{N2} + E_2*X_{CO2}) \quad [6]$$

10

. Step 26 is calculating the constants (A_2, B_2, ...), to obtain a new set of constant values at that state.

Step 27 is repeating the speed of sound measurement at a third thermodynamic state, P_3, T_3, to yield a third

15   independent molecular weight expression:

$$MW = (A_3 + B_3/S_3 + C_3/S_3{}^2) * (1 + D_3*X_{N2} + E_3*X_{CO2}) \quad [7]$$

Step 28 is calculating the constants (A_3, B_3, ...), to

20   obtain a new set of constant values at the third state.

Step 29 is using the three molecular weight equations to solve for the diluent concentrations. Equations [5] and [6] may be equated to eliminate molecular weight and to solve for the concentration of

25   nitrogen, X_{N2}, in terms of the carbon dioxide concentration.

$$X_{N2} = \frac{\left(A_2 + \dfrac{B_2}{S_2} + \dfrac{C_2}{S_2{}^2}\right)(1 + D_2 X_{CO2}) - \left(A_1 + \dfrac{B_1}{S_1} + \dfrac{C_1}{S_1{}^2}\right)(1 + D_1 X_{CO2})}{E_1\left(A_1 + \dfrac{B_1}{S_1} + \dfrac{C_1}{S_1{}^2}\right) - E_2\left(A_2 + \dfrac{B_2}{S_2} + \dfrac{C_2}{S_2{}^2}\right)} \qquad [8]$$

Similarly, Equations [6] and [7] may be equated to eliminate molecular weight and obtain a second equation for nitrogen concentration:

5

$$X_{N2} = \frac{\left(A_3 + \frac{B_3}{S_3} + \frac{C_3}{S_3^2}\right)(1 + D_3 X_{CO2}) - \left(A_2 + \frac{B_2}{S_2} + \frac{C_2}{S_2^2}\right)(1 + D_2 X_{CO2})}{E_2\left(A_2 + \frac{B_2}{S_2} + \frac{C_2}{S_2^2}\right) - E_3\left(A_3 + \frac{B_3}{S_3} + \frac{C_3}{S_3^2}\right)} \qquad [9]$$

Then, by eliminating X_{N2} in the two preceding equations, the carbon dioxide concentration, X_{CO2} , may be expressed in terms of the three measured speeds of sound. That is, the carbon dioxide concentration is expressed

10 as:

$$X_{CO2} = \frac{\left[\left(A_1 + \frac{B_1}{S_1} + \frac{C_1}{S_1^2}\right)\left[\left(A_2 + \frac{B_2}{S_2} + \frac{C_2}{S_2^2}\right)(E_2 - E_1) + \left(A_3 + \frac{B_3}{S_3} + \frac{C_3}{S_3^2}\right)(E_1 - E_3)\right] + \left(A_2 + \frac{B_2}{S_2} + \frac{C_2}{S_2^2}\right)\left(A_3 + \frac{B_3}{S_3} + \frac{C_3}{S_3^2}\right)(E_3 - E_2)\right]}{\left[\left(A_1 + \frac{B_1}{S_1} + \frac{C_1}{S_1^2}\right)\left[\left(A_2 + \frac{B_2}{S_2} + \frac{C_2}{S_2^2}\right)(E_1 D_2 - E_2 D_1) + \left(A_3 + \frac{B_3}{S_3} + \frac{C_3}{S_3^2}\right)(E_3 D_1 - E_1 D_3)\right] + \left(A_2 + \frac{B_2}{S_2} + \frac{C_2}{S_2^2}\right)\left(A_3 + \frac{B_3}{S_3} + \frac{C_3}{S_3^2}\right)(E_2 D_3 - E_3 D_2)\right]} \qquad [10]$$

The value of X_{CO2} may then be calculated, using the calculated constant values and the three measured values

15 of speed of sound. This value may then be substituted into either of the nitrogen equations to obtain the value of X_{N2}. Then, the values of X_{CO2} and X_{N2} may be substituted into Equation [1], [2] or [3] to obtain the value of the test gas molecular weight, MW.

20

Diluent Measurement System

FIGURE 3 illustrates a two-channel diluent measurement system 300, with which up to four different speed of sound measurements at predetermined and
5 measurable pressures and temperatures may be obtained. System 300 uses two speed of sound sensors 306, one on each of two channels. On each channel, two cascaded pressure regulator valves 302 and 303 and a switched bypass valve 304 are used to change the pressure in the
10 channel.

Each channel operates independently at two different selectable pressures from a common gas supply source. On each channel, the selectable pressures are preset by the two pressure regulator valves 302 and 303 arranged in
15 cascade with the lower pressure regulator 302, located downstream of the higher pressure regulator 303, shunted by a solenoid-operated bypass valve 304. With this arrangement, the pressure conditions in each measurement channel can be quickly and automatically changed from
20 high to low pressure and vice versa, without interaction between the two channels.

One of the measurement channels (Channel 1) operates at the system ambient temperature. The other channel (Channel 2) has an electric heater 305 as part of the
25 speed of sound test chamber 306 to raise the temperature of the gas in that chamber above the system ambient temperature.

An example of a suitable speed of sound sensor 306 is described in U.S. Patent Application Serial No.
30 10/406,518, entitled "Device for Precision Measurement of Speed of Sound in a Gas" and incorporated by reference

herein. The speed of sound sensor described therein has a self-contained capillary flow channel made as an intimate part of the chamber for the purpose of equilibrating the gas temperature to that of the chamber

5   prior to measuring the speed of sound.

Both channels of system 300 may be operated with gas flowing through the speed of sound sensors 306, provided that the flow rate does not prevent the gas temperature from equilibrating to the chamber temperature. If a

10   carbon dioxide sensor 307 is desired, it may be located at the exit metering valve 309 of the ambient-temperature speed of sound test channel.

The pressure and temperature test conditions in each measurement channel are relatively arbitrary, but are

15   within the limits for reliable measurement of speed of sound (typically above a few atmospheres pressure or higher). The pressure and temperature values also are sufficiently different to provide adequate differences among the two (or three or four) thermodynamic states

20   used in the test measurements in order to provide distinctive and independent results in the measured speed of sound values and in the subsequent calculations of the diluent gas concentrations and molecular weight. The temperatures in the measurement channels may likewise be

25   relatively arbitrary provided that the heated channel temperature is sufficiently higher than the ambient temperature channel so as to have an independent influence on the measured speeds of sound. The temperatures in the two measuring channels may actually

30   change with time to track any changing ambient temperature conditions caused by variations in

environmental temperature at the system installation.

Examples of suitable pressures and temperature ranges for the two measurement channels are:

Channel No.1:   Channel No. 2:

5   75 psia $< P_1 <$ 1400 psia   75 psia $< P_2 <$ 1400 psia

deg F $< T_1 = T_{amb} <$ 120 deg F $T_2 = T_{amb} + 40$ deg F

An advantage of the three-state measurement method is that the sensing requirements only involve the

10 measurement of speed of sound at the various preset and accurately measured pressures and temperatures. No other gas sensors are required and the amount of heat energy added to the gas in the heated channel is not required to be known. Likewise, the gas flow rates in the two

15 measuring channels, although preferably set to be approximately equal, may be different from one another and are not required to be known.

Processing unit 310 receives speed of sound, temperature, and pressure measurement from the

20 corresponding sensors of FIGURE 3. These inputs are used to calculate only nitrogen or both nitrogen and carbon dioxide concentrations, in accordance with the two-state or three-state methods described above. Processing unit 310 is programmed in accordance with the methods

25 described above. For determining the constant values, processing unit 310 may include a look up table of reference gases and pre-calculated sound speed values as described above, so that the constant values may be determined. Alternatively, processing unit 310 may

30 include stored reference gas compositions and programming for determining sound speed values for the reference

gases at the measured temperature and pressure, so that the constants may be determined.

If the three-state inferential method does not provide sufficient accuracy in resolving the individual

5   concentrations of the carbon dioxide and molecular nitrogen diluent gases, carbon dioxide sensor 307 may be used to constrain the concentration, X_{CO2}, as a means for determining the concentration of molecular nitrogen, X_{N2}, with acceptable accuracy. In this case, the speed of

10 sound measurements are required at only two independent energy states in the test gas sample.

The methods described above take the two diluent gases into separate consideration in order to develop the underlying principles for measurements that potentially

15 do not require a measurement of carbon dioxide. If the two diluent gases are not accurately separable by these relationships, substituting a measured value of X_{CO2} into either of the nitrogen equations to obtain the concentration of molecular nitrogen, X_{N2}, may not yield a

20 suitably accurate result. In that case, an alternate approach is to reformat Equations [1], [2], and [3], with X_{CO2} and X_{N2} merged into a single "combined" diluent gas parameter, X_{DIL}, which represents the total diluent gas concentration. By eliminating MW among the equations as

25 before, a value for X_{DIL} can be obtained. Subtracting the measured value of X_{CO2} from X_{DIL} will yield the concentration of molecular nitrogen, X_{N2}, with a derived value potentially more accurate than that obtainable with the diluent concentration formulas involving separate gas

30 constituent terms.